PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

β-Aluminium Fluoride

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel form of aluminium fluoride and to a process for its preparation.

Aluminium fluoride has been known for many years. Recently it has achieved importance because of its utility as a catalyst in various organic vapour-phase reactions, notably that of the reaction between acetylene and hydrogen fluoride to form vinyl fluoride and 1,1-difluoroethane. Such a process is described in U.S. Specification No. 2,471,525.

Aluminium fluoride has several polymorphic forms. That which has been previously known is the high-temperature stable form, and this has been named α-aluminium fluoride by analogy with the high-temperature stable form of alumina.

We have now discovered a method for the preparation of another form of aluminium fluoride which we call β-aluminium fluoride by analogy with the corresponding form of aluminium oxide. This form of the fluoride has not been previously described or isolated.

According to one embodiment of the present invention we provide a process for preparing B-aluminium fluoride which comprises dehydrating α-aluminium trifluoride trihydrate at a temperature of from 150 to 450°C. until water ceases to be evolved therefrom.

The new β-form of aluminium fluoride is different from the α-form and the two are readily distinguished by X-ray analysis of the crystals. The X-ray diffraction pattern of α-aluminium fluoride is given on ASTM Card 9—138. α-Aluminium fluoride belongs to space group D_3^7—R32, has unit cell parameters a=4.927Å and c=12.445Å, a unit cell volume of 2516Å^3, contains six molecules of aluminium fluoride per unit cell and has a calculated density of 3.197 g./cc. The new β-form of aluminium fluoride belongs to space group D_{6h}^4—P6/mmc, has unit cell parameters a=6.93Å and c=7.125Å, a unit cell volume of 2964Å^3 and has a calculated density of 2.815 g./cc.

In accordance with the invention the method for preparing catalytically active β-aluminium fluoride consists in dehydrating α-aluminium fluoride trihydrate at 150—450°C. At least 150° is preferred to decompose the hydrate. Temperatures above 600° cause the formation of major amounts of α-aluminium fluoride. At temperatures above 500° α-aluminium fluoride begins to form. Care should be taken that α-aluminium trifluoride trihydrate is not converted to the β-form during precipitation or the resulting β-aluminium fluoride will not be pure.

α-Aluminium trifluoride trihydrate is prepared by the method described by Ehret and Frere in J. Amer. Chem. Soc., *67*, 64 (1945). More specifically, alumina or aluminium is dissolved in hydrofluoric acid near 10—15°C. and a hydrate precipitates. This hydrate, $AlF_3.9H_2O$ loses water on standing in air to form α-$AlF_3.3H_2O$. α-Aluminium trifluoride trihydrate is easily characterised by its X-ray diffraction pattern which also distinguishes it from β-aluminium fluoride trihydrate. The α-hydrate belongs to space group D_{3d}^5—R3m, has unit cell parameters a=9.272Å and c=4.647Å and contains three molecules per unit cell. Its X-ray diffraction pattern is given in Table I. The X-ray diffraction pattern of the β-trihydrate is given on ASTM Card 9—108.

The X-ray diffraction lines of the α-aluminium trifluoride trihydrate and β-aluminium fluoride are given herebelow.

TABLE I

Spacing and Intensities of α-$AlF_3.3H_2O$

d_c(Å)	Relative Intensities *	(hkl)
4.637	100	(110)
4.046	46	(101)
3.048	1	(201)
2.676	4	(300)
2.547	36	(211)
2.318	2	(200)
2.248	7	(102)
2.023	5	(202)
2.011	5	(311)
1.854	22	(212)
1.845	22	(401)
1.752	2	(410)
1.714	6	(321)
1.614	11	(312)
1.561	$<<1$	(003)
1.546	<1	(330)
1.524	2	(402)
1.519	2	(501)
1.480	<1	(113)
1.448	4	(322)
1.444	4	(421)
1.378	1	(511)
1.349	3	(303)
1.338	3	(600)
1.295	1	(223)
1.286	3	(520)
1.274	<1	(422)
1.270	<1	(431)
1.186	2	(104)
1.166	1	(413)
1.159	3	(440)

* Based on the 4.637Å line having an intensity of 100.

TABLE II

Spacings and Intensities of β-AlF_3

d(Å)	Intensity	(hkl)
6.002	vst	(100)
3.563	vst	(002)
3.465	st	(110)
3.063	w	(102)
3.001	st	(200)
2.484	w	(112)
2.295	w	(202)
2.266	w	(210)
2.209	w	(103)
2.161	w	(211)
2.001	m	(300)
1.914	m	(212)
1.782	mst	(004)
1.732	mst	(220)
1.708	mw	(104)
1.665	m	(310)
1.585	mw	(114)
1.558	mw	(222)
1.532	m	(204)
1.500	m	(400)
1.377	mw	(320)
1.330	w	(304)
1.310	vw	(410)
1.284	w	(322)
1.242	w	(224)
1.216	w	(314)
1.200	vw	(500)
1.188	vw	(006)
1.148	mw	(404)
1.134	w	(420)

St = strong, m = medium, w = weak, v = very.

In order that the invention may be more fully understood the following Example is given by way of illustration only.

EXAMPLE

A mixture of 660 g. of distilled water and 550 g. of 48% hydrofluoric acid was prepared in a polyethylene beaker and the solution cooled to 5°C. Then 312 g. of hydrated alumina "Alcoa" (trade mark) C—33 grade from the Aluminum Company of America) was added in small portions to the acid solution, maintaining the temperature during the addition below 10°C. When the alumina addition was complete, the mass was agitated overnight in an ice bath. The precipitate which formed was collected on a chilled filter and the solids were washed with cold water. After air drying, the solids were dried at 100°C. for four hours and finally in a muffle furnace at 400°C. for four hours. The product was identified as β-aluminium fluoride by its X-ray diffraction pattern.

WHAT WE CLAIM IS:—

1. β-Aluminium fluoride.

2. A process for preparing β-aluminium fluoride which comprises dehydrating α-aluminium trifluoride trihydrate at a temperature from 150°C. to 450°C. until water ceases to be evolved therefrom.

3. A process for preparing β-aluminium fluoride substantially as herein described in the Example.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn, London, W.C.1.
For the Applicants.

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